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DEVELOPMENT OF A HYDRAZINE/NITROGEN DIOXIDE FIBER OPTIC SENSOR

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ABSTRACT

A simple, low cost fiber optic sensor is described for the simultaneous vapor phase detection of hydrazines and nitrogen dioxide. The device utilizes an acid-base indicator that undergoes color changes depending on which gas is present. The indicator is imbedded in a hydrogel matrix to aid long-term stability. The sensor responds in less than one minute to hydrazine (50 ppm) and nitrogen dioxide (400 ppm). Stability over times greater than several days remains to be tested. The sensor should be ideal for long-term detection of leaks in propulsion systems utilizing hypergolic propellants especially since explosion hazard due to spark is a concern.

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1. INTRODUCTION

Hydrazine and monomethylhydrazine (fuels) and dinitrogen tetroxide (oxidizer) are hypergolic propellants that are used in the Space Shuttle and other spacecraft guidance systems and several types of military missiles. These hypergols form hazardous gases that are toxic to humans at low concentrations and are flammable and explosive at higher concentrations. The recommended exposure limits are 0.01 ppm for hydrazine (HZ), 0.01 ppm for monomethylhydrazine (MMH) and 3 ppm for nitrogen dioxide (NO_2), the dissociation product of dinitrogen tetroxide.[1] The lower explosion limits in air at atmospheric pressure are 2.9% for HZ and 2.5% for MMH.[2,3] Therefore, leak detection of these chemicals is very important.

The ideal sensor for leak detection should meet the following requirements. To avoid the risk of explosion, electrical devices should not be used. The sensor should be capable of identifying which gas is leaking. Although high sensitivity is an attribute, for leaks in contained spaces where toxicity is not a concern (e.g., the interior of a missile), detection at higher concentrations is both necessary and sufficient. Especially for applications to missiles that are stored for periods of years, long-term stability of the sensor is critical. Finally, the ideal sensor should be simple, increasing its reliability, and low cost.

A variety of sensors are currently in use for the detection of hydrazines and nitrogen dioxide.[4] Electrochemical detection of hydrazines (ppb) and NO_2 (ppm) is a common method (e.g., Interscan Corporation). In addition to the electrical danger, however, a separate device is required for each gas, increasing the inherent cost and size. Simultaneous detection by solid-state devices such as gold-doped tungsten oxide and titanium dioxide has been suggested[5-8] but these detectors require elevated temperatures (100-800°C) and are therefore unsafe when combustible gases may be present. They also are unselective to a wide variety of gases. Other sensors for hydrazines are coulometric[9] (based on reaction with bromine) colorimetric (based on reaction of hydrazines with p-dimethylamino-benzaldehyde[10] or the reversible reaction with pH sensitive triphenylmethane dyes[11]) or fluorescent[12] (based on reaction with aromatic dicarbaldehdyes).

We describe the use of a fiber optic sensor, employing light rather than electricity to minimize explosion hazards. We take advantage of the acid-base properties of the hypergols using indicators that change color with pH to distinguish NO_2 from the hydrazines. The relevant chemical reactions are listed below. Dinitrogen tetroxide is in equilibrium with nitrogen dioxide:

$$N_2O_4 \rightleftharpoons 2\,NO_2 \tag{1}$$

Nitrogen dioxide in turn reacts with water to form an acidic solution (nitric acid) and nitric oxide:

$$3\,NO_2 + H_2O \rightarrow 2\,H^+ + 2\,NO_3^- + NO \quad (acid) \tag{2}$$
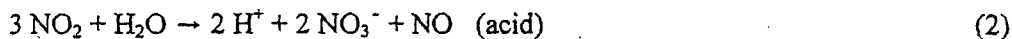
On the other hand, hydrazine forms a basic solution with water:

$$N_2H_4 + H_2O \rightarrow N_2H_5^+ + OH^- \quad (base) \tag{3}$$

Incorporating the indicator in a hydrophilic polymer matrix (hydrogel) should inhibit evaporation of water and give stability to the sensor over a long period of time. Although commercial fiber optic pH sensors are available (Ocean Optics), these probes are expensive, involving a spectrophotometer and computer, and are designed for solution rather than gas phase measurements.

2. EXPERIMENTAL

A. Description of the First-Generation Prototype Sensor

This sensor was designed for measurements on solutions that had been exposed to gases but not as a direct gas probe. A jar (2.75 in diam, 3.5 in tall) with a flat mirror (30 mm diam) glued to the inside bottom contained the indicator (Figure 1). The optical sensor consisted of two 1 mm jacketed plastic fiber
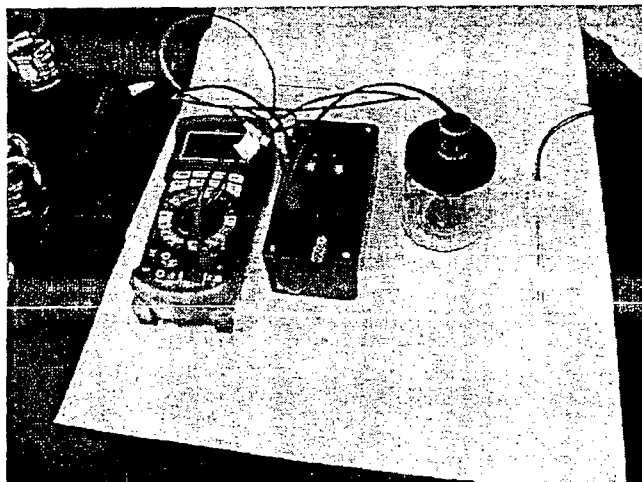

Figure 1. Sensor system (left to right: DMM, electronics box, first and second-generation sensors)

optic cables (Digi-Key A1700-5-ND) that passed through the top of the jar and were enclosed by heat shrink tubing with a 2 mm diameter wooden rod for rigidity. The sensor tip was positioned about 20 mm above the mirror. Light from a red LED (Industrial Fiber Optics IF-E97, peak wavelength 660 nm) was carried by one of the optical fibers. The reflected light was detected through the second fiber by a photodiode (Industrial Fiber Optics IF-D91, maximum photosensitivity 850 nm). The LED and photodiode were each contained in PVC housing with a cinch nut to hold the fiber optic cable in place. Schematics of the two electrical circuits are shown in Figure 2. The LED required a 360-ohm resistor with a 9-volt battery. The photodiode required a 1-mega ohm resistor between the output leads to the voltage meter along with a 9-volt battery. All the electronics were contained in a plastic box that was connected at some distance to the sensor solely by the fiber optic cables. The photodiode output was read with a Wavetek Model 235 digital multimeter (DMM).
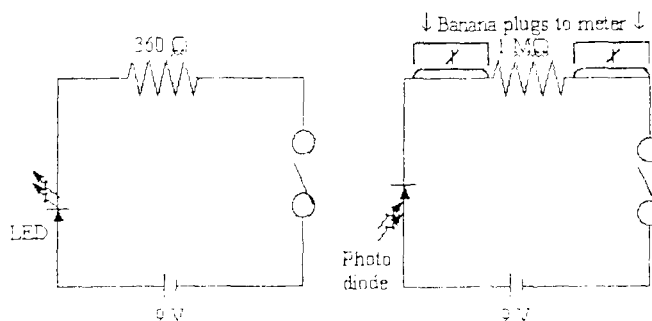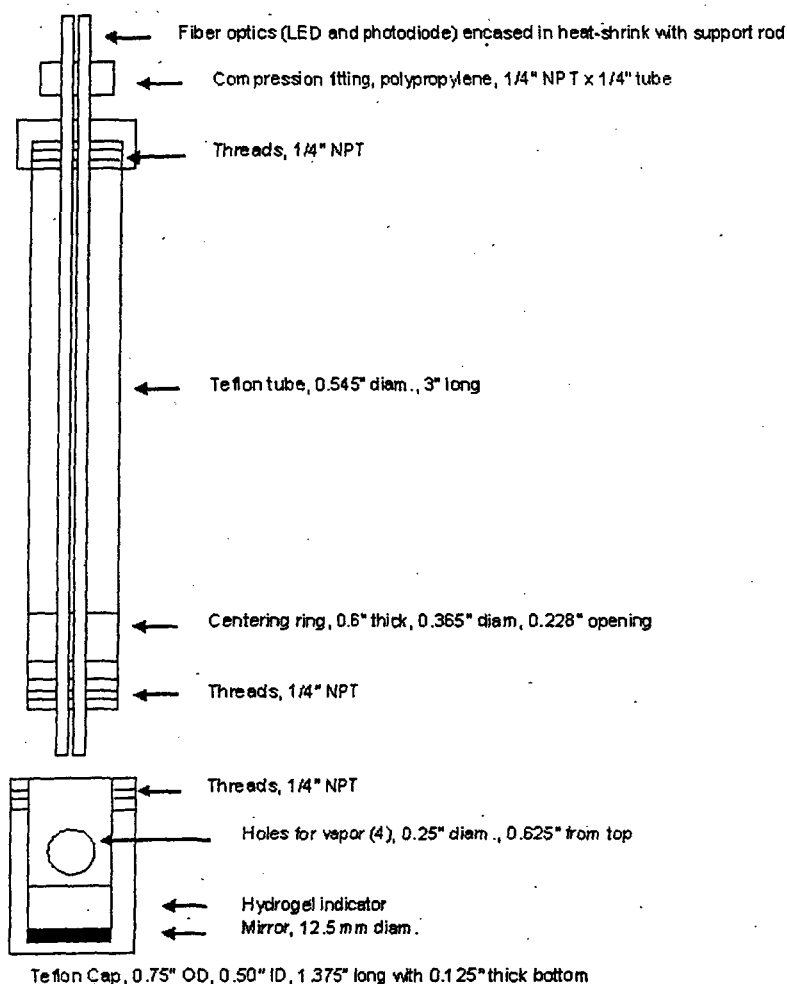

Figure 2. Circuit diagrams for LED and photodiode

B. Description of the Second-Generation Prototype Sensor

A fiber optic probe was constructed as shown in Figures 1 and 3. The reflecting surface in the Teflon cap was the backside of an aluminized 12.5 mm diam mirror, 2 mm thick (Edmund Industrial Optics NT32-942). The glass protected the aluminized surface and was flat (4-6 wave) so distortion of the beam was avoided. Two to three drops of the indicator/hydrogel mixture were placed on the mirror and allowed to flow evenly over the surface. The hydrogel sealed the edges of the mirror and provided additional protection of the aluminum surface from the corrosive gases. The same LED, photodiode, and associated electronics described above were connected to the probe by its fiber optic cables.

Coarse adjustment of the fiber position was made using the compression fitting at the top of the sensor with the cap screwed in about half way. The fiber distance from the mirror was optimized after each new sample was introduced by screwing the cap in or out to give the maximum signal. The mirror could be removed by tapping the cap on the bench or by inserting a small flat spatula along the edge of the mirror

Fiber optics (LED and photodiode) encased in heat-shrink with support rod

Compression fitting, polypropylene, 1/4" NPT x 1/4" tube

Threads, 1/4" NPT

Teflon tube, 0.545" diam., 3" long

Centering ring, 0.6" thick, 0.365" diam, 0.228" opening

Threads, 1/4" NPT

Threads, 1/4" NPT

Holes for vapor (4), 0.25" diam., 0.625" from top

Hydrogel indicator
Mirror, 12.5 mm diam.

Teflon Cap, 0.75" OD, 0.50" ID, 1.375" long with 0.125" thick bottom
By: Rebecca Young, Clayton Baum, Steve Parks
Date: 06/19/02   Scale: 5:4

Figure 3. Fiber optic probe

C. Preparation of the Acid-Base Indicators

Preparation of the indicators (Figure 4) followed the instructions in the Handbook of Chemistry and Physics[13]. Specifically, 0.1 g Mallinckrodt indicator grade thymol blue (TB) was dissolved in 21.5 mL 0.01 M NaOH plus 228.5 mL water; 0.1 g Kodak reagent grade bromophenol blue (BP), sodium salt, was dissolved in 15 mL 0.01M NaOH plus 235 mL water; 0.1 g Aldrich A.C.S. reagent grade bromocresol green (BG), water soluble, was dissolved in 14 mL 0.01 M NaOH plus 236 mL water; 0.1 g Baker Analyzed Reagent bromothymol blue (BT), sodium salt, was dissolved in 16 mL 0.01 M NaOH plus 234 mL water. Universal Indicator Solution (UI) was purchased from Fisher Scientific and contains the following dyes: phenolphthalein, thymol blue, methyl red and bromothymol blue. Concentrations reported later are percent by volume of these standard solutions added to water or hydrogel.
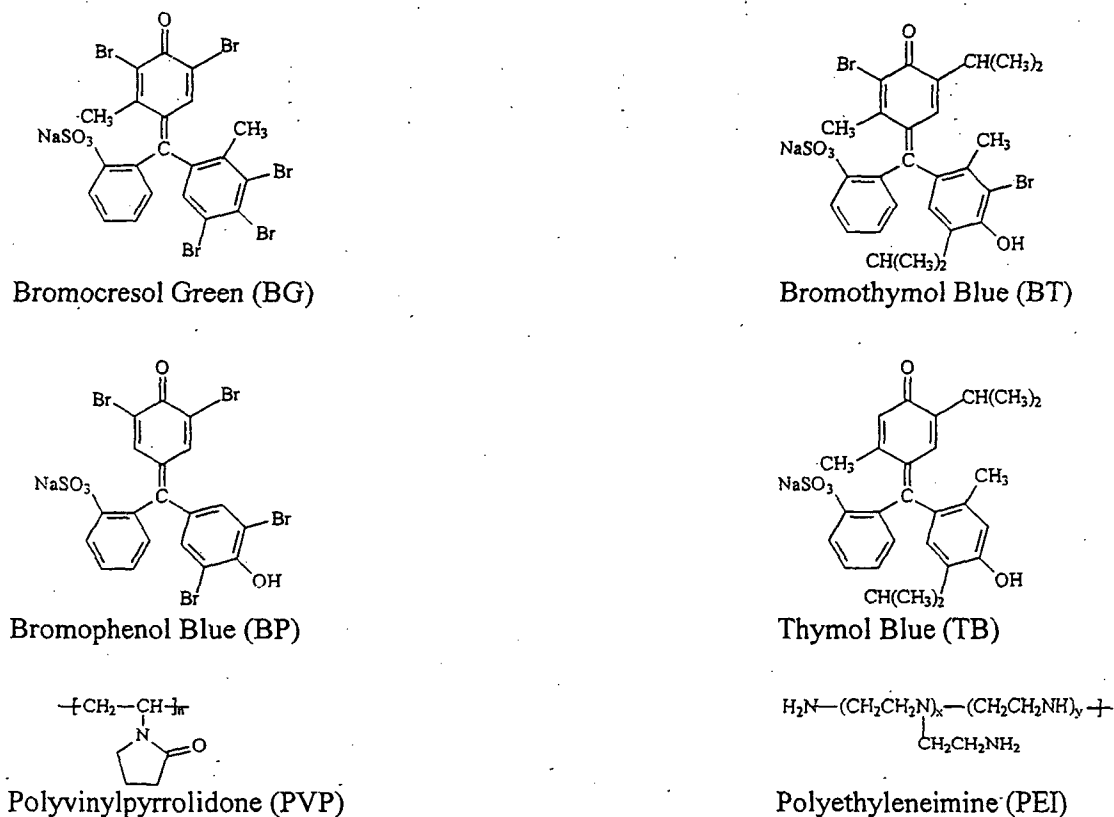
Bromocresol Green (BG)

Bromothymol Blue (BT)

Bromophenol Blue (BP)

Thymol Blue (TB)

Polyvinylpyrrolidone (PVP)

Polyethyleneimine (PEI)

Figure 4. Molecular structures of indicators and hydrogel components

D. Preparation of the Hydrogel Matrix

The hydrogel chosen because of its ease of preparation was Aquatrix II marketed by Hydromer, Inc. This hydrogel is a mixture of two polymers (Figure 4). Part A (Product Code 1CQA01) is polyvinylpyrrolidone (PVP) and Part B, High Tack (Product Code 1CQA07) is polyethyleneimine (PEI). Part B includes glycine as an additive to help retain water. The two components can be mixed in a variety of ratios. Ratios of Part A/Part B ranging from 4/1 to 1/3 were tested and the 1/1 ratio provided the best penetration of the hydrazines and NO_2.

The PEI has a pH of 9.2. Before mixing with Part A, Part B was neutralized by adding 1 drop of 1.76 M

sulfuric acid to approximately 4 mL of PEI. At a pH of 7, Part B is clear; excess or deficient acid results in a cloudy liquid. The pH was confirmed with Hydrion Paper, Micro Essential Laboratory (range of 1 to 11). The neutralized hydrogel initially was less viscous than the hydrogel without neutralization but thickened over time. The indicator solution generally was mixed with Part A before forming the hydrogel. Similar results were obtained, however, by adding the indicator to the hydrogel mixture. Aquatrix II sticks to most surfaces including glass and cannot be removed without distorting the gel; it does not stick to Teflon. After testing, the hydrogel was removed by flushing the cap with deionized water. If the hydrogel hardened, removal required soaking the cap in water for about 1 hour.

E. Generation of the Gases

Anhydrous HZ, MMH and NO_2 vapors were produced using Span Pac 361 Precision Standard Generators (Kin-Tek Laboratories, Inc.) that incorporate Teflon permeation tubes for the hydrazines and heated steel cylinders containing liquid N_2O_4 for the NO_2. Dry air was used as the carrier gas at a flow rate of 2 L/min. The calibrated concentrations were 52 ppm for HZ, 17 ppm for MMH and 56 ppm for NO_2. An Air Liquide cylinder of 4000 ppm NO_2 in N_2 was used for most of the NO_2 experiments. The flow rate was varied and the mixture could be diluted further with dry N_2. The CO_2 was standard grade.

3. RESULTS AND DISCUSSION

As the color of the indicator changes, the amount of red light transmitted by the indicator changes and the detector signal should change. If the indicator is red (absorption in the blue region) then more red light is reflected off the mirror and the detector voltage signal should be high. If the indicator is blue (absorption in the red region) less red light is reflected so the signal should be low.

A. First generation sensor
1. Opaque materials

Initial studies showed that the sensor responds to differences in the colors of opaque materials such as colored tape (yellow, 80 mV; red, 76 mV; green, 15 mV) and pH paper (air, orange, 74 mV; hydrazine, green, 40 mV; sulfuric acid, red, 73 mV). Note that yellow absorbs less of the LED light than red and that there is very little distinction between red and orange. Thus, the indicator in the pH paper would not be useful in distinguishing NO_2 from the CO_2 in air using the red LED.

2. Solutions

Samples in vials or beakers were exposed by placing them in a polypropylene container and directing the gas at the sample through tubing in the top of the container. There was good reproducibility (< 10% variation) when solutions filled the sensor jar to a level above the mirror. However, when solutions or hydrogels were kept in vials placed on the mirror the variation was sometimes greater than 100% depending on the position of vial. The reason is that the bottom of the container was not uniform, affecting the transmission of the light. Typically, a minimum of six trials was performed when using the vials, changing the position for each trial. Significant results were obtained as reported below.

An initial selection of indicators was based on the change in their wavelength of maximum absorption with pH[14]. Although the pH depends in part on the concentration of the dissolved gas, the approximate pH values are hydrazine 11, carbon dioxide 5, and nitric acid < 2. The indicator should absorb strongly at the wavelength of the LED for one gas (e.g., hydrazines) but not the other (e.g., nitrogen dioxide) and there should not be interference by other gases, specifically carbon dioxide. TB shifts from 596 nm to 430 nm as the pH goes from 9.6 to 8.0 and from 430 nm to 544 nm as the pH goes from 2.8 to 1.2. It gives a very rapid response (< 1 min) to both HZ and NO_2. However, TB is sensitive to CO_2, changing

from green to red/orange overnight. Thus, there is not much further change when TB is exposed to NO_2; in fact, there is a decrease in signal so it is hard to distinguish from exposure to HZ. Likewise, UI is affected by CO_2 so there is not much change (yellow to red) upon exposure to NO_2. BP shifts from 592 nm to 436 nm as the pH goes from 4.6 to 3.0, but its response to NO_2 is relatively slow and there is no response to HZ. BT shifts from 617 nm to 433 nm as the pH goes from 7.6 to 6.2. BT is already dark green at neutral pH so there is not much change with HZ, although it is rapid. However, BT is the indicator of choice to distinguish HZ if CO_2 is a problem because it is yellow below a pH of 6. BG shifts from 617 nm to 444 nm as the pH goes from 5.6 to 4.0. It shows rapid response and large color change (blue to yellow) when exposed to NO_2. A 10%TB/BG (3/1) solution was the best combination of indicators with the best indicator ratio and concentration for observing a relatively large (7 mV) change for both acid and base. It responds to HZ and MMH (1-2 mV/min) and NO_2 (13 mV/min at 4000 ppm, 2 mV/min at 400 ppm, 0.1 mV/min at 56 ppm). A summary of the indicator results is given in Table 1.

Indicator	HZ	NO$_2$	Disadvantage
Thymol blue	rapid	rapid	Sensitive to CO_2; no response to HZ in hydrogel
Bromophenol blue	none	slow	
Bromothymol blue	rapid	rapid	Sensitive to CO_2; small color change with HZ
Bromocresol green	none	rapid	

Table 1. Indicator response

3. Hydrogels

Although 10% TB in solution responds quickly to HZ, 12% TB in hydrogel (Part A/Part B, 1/1) showed no visual change after 10 min exposure to HZ. In contrast, 12% BT in hydrogel (1/1) turned blue to a depth of 1 mm below the surface after 1 min of HZ while the rest of the hydrogel mixture remained green. Thus BT is much better than TB in HZ response even though in solution TB gives a more dramatic color change. In hydrogel (4/1), 6% BT produced only a 0.5 mm depth of blue after 1 min exposure to HZ which darkened over 10 min of exposure. In hydrogel (1/3), 13% BT produced only a 0.5-1 mm depth of blue after exposure to HZ. Thus, a 1/1 ratio for hydrogel seems to be best for penetration of the gas although it is only to a depth of 1 mm. This implies that a thin film no more than 1 mm should be used. Several hours after exposure, the blue color diffused throughout the sample to give a darker green. Exposure of 16% BT in hydrogel (1/1) to NO_2 (4000 ppm) produced a 0.5 mm depth of pale green-yellow in 1 min extending to a 2 mm depth of yellow in 10 min of exposure. The sensor response was 22 ± 1 mV for the indicator alone, 18 ± 6 mV after 10 min exposure to HZ, and 48 ± 17 mV after 10 min exposure to NO_2. A 16% mixture of BT/BG (1/1) in hydrogel (1/1) also showed a change from blue to darker blue to a depth of 1 mm) in 1 min exposure to HZ and blue to pale blue-green to yellow (5 min) to a depth of 1 mm after 1 min exposure to NO_2 (4000 ppm).

B. Second generation sensor
1. Solutions

The development of the sensor probe allowed much more accurate measurements in a real time mode. The probe was placed through a hole cut in the top of a polypropylene container. The top also contained a tube through which the gas flowed into the container. After optimizing the distance between the optical fibers and the mirror, readings were taken with no gas flow to establish a baseline. BT alone (40%) with a solution depth about 2 mm gives very good response (Table 2). The readings and change in readings are higher than for the first generation sensor and the response time is faster. The sensor detects NO_2 at 10 ppm in less than 1 min and senses this gas even at 0.005 L/min (almost static conditions). It also

responds well to HZ. However, BT is sensitive to carbon dioxide.

Readings in mV					
Exposure	0 min	1 min	5 min	10 min	Average
No Gas	164	164	164		
Hydrazine, 52 ppm	164	164	155	125	4 mV/min
New Sample, No Gas	158	162	171	184	2 mV/min
NO_2, 4000 ppm, 0.005 L/min	186	188	217	288	10 mV/min
New sample, no gas	100	100	100		
NO_2, 40 ppm, 2.8 L/min	100	106	131	181	8 mV/min
New Sample, No Gas	120	120	120		
NO_2, 10 ppm, 2 L/min	120	129	149		5 mV/min

Table 2. Response of BT in Solution to HZ and NO_2

2. Hydrogels

In contrast to solution, BT in hydrogel senses NO_2 only at high concentration (4000 ppm but not 400 ppm) and high flow rate (> 0.1 L/min), but it is not as sensitive to CO_2. Blowing CO_2 on BT in solution turns the color to yellow in about 15 seconds; there is no visual effect on BT in hydrogel even after 30 min. Increasing the concentration of BT in hydrogel from 16% to 50% improves the response. The increased fluidity allows a thinner layer of indicator to be deposited on the mirror. No additional improvement occurs at still higher concentrations up to 84% BT. Solid BT dissolved in neutralized hydrogel (0.004g BT in 10 mL) giving a dark green color. However, the response of the sensor was not better than mixtures of the standard BT solution with hydrogel. The optimal sensor to date is a BT/BG (1/1) mixture, 50% in hydrogel, that is deposited in a very thin coat, less than 1 mm. The results are shown in Table 3. This sensor detects HZ at 52 ppm and NO_2 at 4000 ppm under near static conditions and 400 ppm at a flow rate close to that of HZ. The fact that the response increases as the flow rate increases suggests that there is a pressure buildup in the container housing the sensor that aids in diffusion of the gas into the hydrogel matrix. In solution, the response is fairly independent of the flow rate.

Readings in mV					
Exposure	0 min	1 min	5 min	10 min	Average
No Gas	359	358	352		
Hydrazine, 52 ppm	350	347	326	311	4 mV/min
New Sample, No Gas	376	378	381		
NO_2, 4000 ppm, 0.01 L/min	378	381	394		3 mV/min
NO_2, 4000 ppm, 0.1 L/min	364	369	380		3 mV/min
New Sample, No Gas	370	371	372		
NO_2, 400 ppm, 2.3 L/min	372	380	396		5 mV/min

Table 3. Response of BT/BG (1/1), 50% in Hydrogel to HZ and NO_2

CONCLUSIONS

We have developed a method for simultaneous detection of hydrazines and NO_2 in the vapor phase and have constructed a sensor prototype that gives promising results. The sensor is a simple fiber optic device composed of just a red LED light source, a photodiode detector, fiber optics and a mirror. There are no moving parts, increasing the long-term reliability. The cost, excluding labor, is under $100 so that these sensors can be expendable and used in multiple locations. There is no spark hazard and no electrical noise interference because of the fiber optics. Likewise, the sensor is light and compact, requires low power, and is amenable to remote control.

A range of acid-base indicators has been examined and 10% TB/BG (3/1) and 40% BT were found to provide the best response in solution, while 50% BT/BG (1/1) was best in hydrogel. In solution, the sensor detects HZ (52 ppm), MMH (17 ppm) and NO_2 (10) ppm in less than 1 min and senses NO_2 even at 0.005 L/min (almost static conditions). Diffusion of the gases through the hydrogel matrix is restricted to the top 1 mm reducing the response and leading to the use of films less than 1 mm. Nonetheless, with hydrogel the sensor still detects HZ (52 ppm) and NO_2 (400 ppm) at 2-3 L/min and NO_2 at 4000 ppm at 0.01 L/min. There is no interference from humidity.

Future development includes fine-tuning the indicator ratio and concentration. Other matrices may allow easier penetration of the gases and retain moisture better than the Aquatrix II. The major test is determining the stability of the sensor over time. The plastic fiber and optics must be replaced with silica for longer transmissions distances. An alarm will need to be incorporated set to detect a minimum voltage change per unit time in the positive (NO_2) or negative (hydrazines) direction rather than an absolute voltage. This would eliminate problems with voltage drift over time resulting from a variety of sources such as CO_2, or degradation of the LED, power source, indicator, hydrogel, and optics.

The short-term value to KSC is an increase in the ability to sense the hazardous gases associated with hypergolic propellants, reducing the response time for leak detection and identification and the cost of detection. The long-term value is increased safety at the spaceport and at other sites that make use of these propellants.

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